Spinning Cloth Disc Reactor: Applicability to the Epoxidation of Limonene

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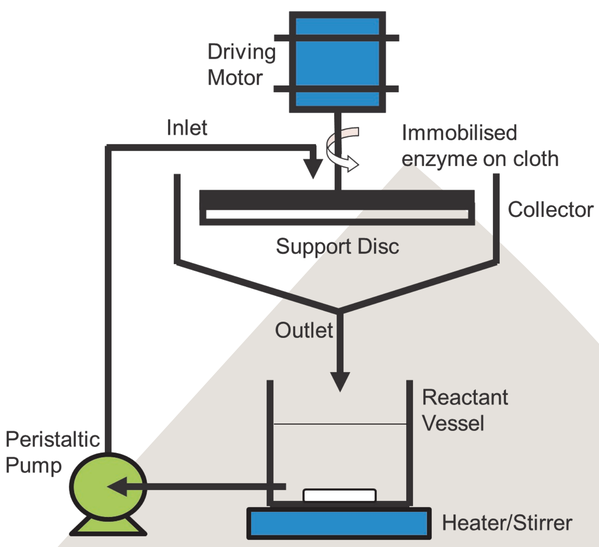
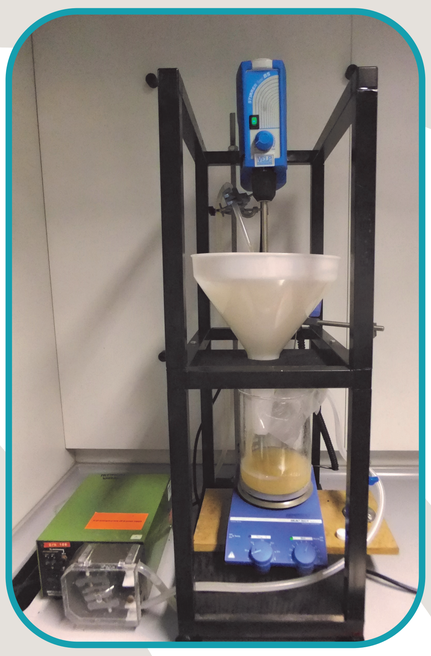
1. Introduction

As the market for bio-based plastics increases, alternative feedstocks need to be found. Limonene, the main constituent of orange peel, is one of these. Its epoxides can be used to produce polycarbonates and polyurethanes,[1,2] but process intensification for producing these epoxides on an industrial scale using a benign method is yet to be investigated.

Process intensification involves the substantial improvement of a manufacturing process, either by improved energy efficiency, cost-effectiveness, or other qualities such as improved reaction rates, reduced waste production and improved purification steps. The spinning cloth disc reactor is a novel reactor suitable for enzyme-catalysed reactions that exhibits properties associated with process intensification. This is the first reported use of the reactor for a multi-step reaction.

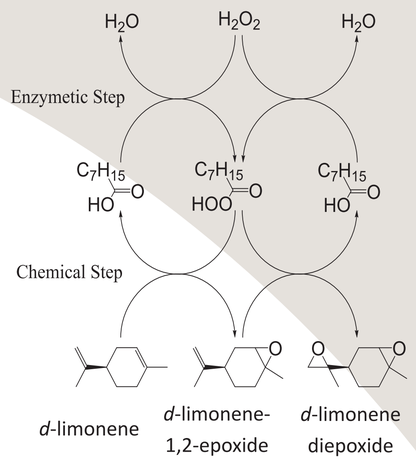
2. Spinning Cloth Disc Reactor





- ✓ Improved mass transfer
- ✓ Rapid mixing
- ✓ Ensures enzyme stability with retention of activity [3]

3. Enzyme-Catalysed Epoxidation of Limonene



- Enzymes require Ser-His-Asp group with an additional carbonyl group in order to catalyse perhydrolysis[4,5,6]
- Most enzymes favour hydrolysis over perhydrolysis as the carbonyl group isn't present

Solution: 470 mL octanoic acid
240 mL limonene
290 mL hydrogen peroxide solution (30 wt%)

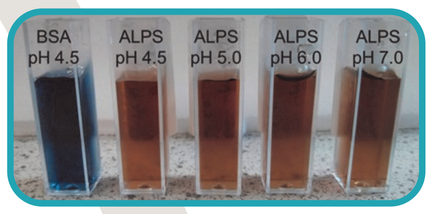
Mass Flow Rate: 1.6 g s^{-1}

Disc Rotation: 50 RPM

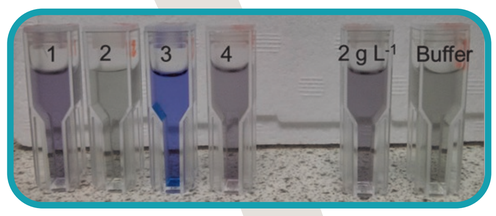
Temperature: 20 °C

Enzyme: amano lipase PS from *B. cepacia*

4. Enzyme Loading



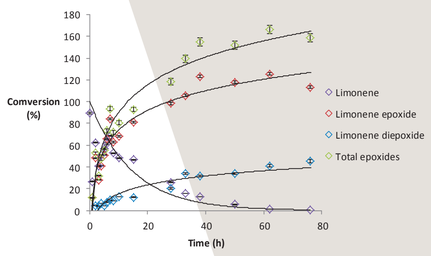
Bradford assay pH tests



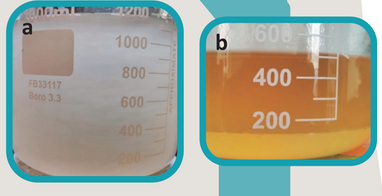
BCA assay tests - solutions 1 and 3 contain PEI

- ✓ Predicted active lipase loading on cloth of 0.23 g based on tributyrin assay lipase activity tests
- ✗ Bradford's assay did not interact with lipase - limited number of amino acids present that interact with the assay
- ✗ BCA assay interacted with chemicals used to immobilise enzyme - PEI has well known metal chelation properties, resulting in false results

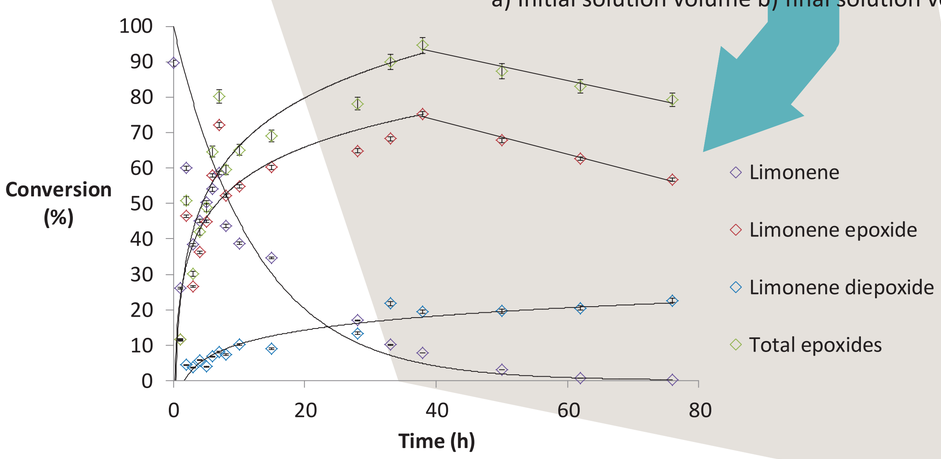
5. Results: Reaction?



Theoretical conversion vs. time without taking volume change into account

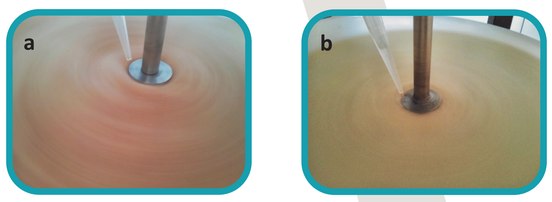


a) Initial solution volume b) final solution volume



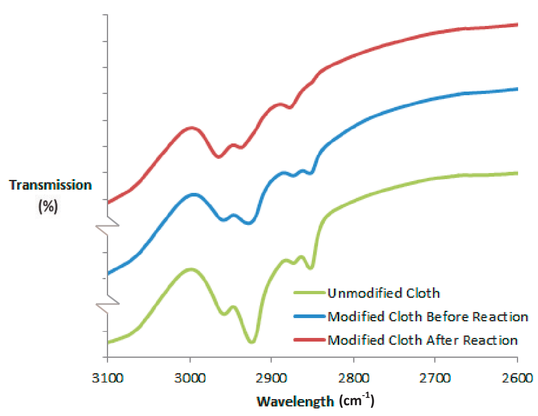
Conversion vs. time based on hydrogen peroxide concentration

6. Effect of Reaction on Cloth



a) Initial colour b) colour after 4 hours 25 minutes

- Cloth bleached by hydrogen peroxide
- FT-IR after 24 hours shows removal of methylene groups present on cloth



Decrease in intensity of methylene groups

7. Conclusions & Future Work

Reaction successfully carried out without solvent, with a total epoxide yield of 95% after 38 hours.

Higher diepoxide yield, 19.4 %, achieved than that reported for batch reaction, 14.6 % after 24 hours.[7]

Investigation into alternative enzyme supports, and potentially immobilisation method, required.

Reactor needs to be redesigned in order to minimise volumetric loss and allow enzyme to function at optimal temperature.

Deconstruction of reaction necessary in order to accurately calculate rate kinetics, with comparisons made to batch reactions.

References

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